

# PATENT SPECIFICATION

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## (54) GLASS AND GLASS-CERAMICS AND COMPOSITIONS THEREFOR

(71) I, KAREL VACLAV DOSTAL, of 8, Stockley Court, Broom Park Estate, Ushaw Moor, Co. Durham, England, a citizen of Czechoslovakia, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions for use in the production of glass-ceramics and glasses, and to the glass-ceramics and glasses obtained therefrom.

The production of glass-ceramic articles by controlled devitrification of glasses containing nucleating agents is well known and has received increasing attention over recent years. The glass-ceramic articles are characterised in general by their strength and hardness, their inertness to chemical, oxidative and atmospheric attack, their heat resistance and low thermal expansion, and their good electrical properties.

In general, the glasses which form the precursors of the glass-ceramic materials are obtained by the fusion of compositions formed from pure oxides or from metallurgical slag, special and often expensive compositions frequently being required for the achievement of certain properties in the glass-ceramic materials.

It has now been found that glass-ceramic materials having very desirable physical and/or chemical properties such as high mechanical strength, high resistance to abrasion and chemical attack, good electrical properties and low thermal expansion characteristics (depending on the actual compositions used) can be obtained from compositions containing fly ash. By "fly ash" is meant fine ash which is obtained from the burning of coal, as exemplified in particular by the fine ash which is obtained from the combustion of pulverised coal, e.g. in coal fired electricity generating plants, and which is carried away by the flue gases in the form of a powder and subsequently recovered from the gases by, e.g., mechanical or electrostatic precipitation. As fly ash is a cheap and

readily available material, the invention provides a route to low cost glass-ceramic materials having desirable physical properties.

According to the present invention there is provided a composition suitable for forming into a glass-ceramic, the composition including the following oxides as essential ingredients:

	by weight	
SiO <sub>2</sub>	30—80%	60
Al <sub>2</sub> O <sub>3</sub>	10—30%	
MgO	0.5—20%	
CaO	0.5—25%	
Fe <sub>2</sub> O <sub>3</sub>	1—13%	
BaO and/or ZnO	1—10%	

and TiO<sub>2</sub> as nucleating agent, optionally together with one or more other nucleating agents;

the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, CaO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and other nucleating agent or agents present, if any, forming at least 90% by weight of the composition, and each oxide being provided as such or in the form of an equivalent amount of at least one precursor therefor, as herein defined; and at least 10% by weight of the composition, calculated as oxides, being provided in the form of fly ash as herein defined.

At the higher end of the range of concentrations specified for SiO<sub>2</sub>, difficulties may be encountered in fusing the compositions. It is therefore preferred to use not more than 70% by weight SiO<sub>2</sub>, the preferred range being 45 to 65% by weight. For similar reasons it is preferred to use not more than 25% by weight Al<sub>2</sub>O<sub>3</sub>, the preferred range being 15 to 25% by weight.

The presence of large concentrations of MgO and CaO in the compositions tend to make the melts corrosive; thus tending to create difficulties in handling. It is therefore preferred to use not more than 21% by weight in total of CaO and MgO, the most preferred range being from 10 to 21% by weight. Within this range, it is particularly preferred to use from 1 to 6% by weight of one of MgO or CaO with from 8 to 15%

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by weight of the ther f CaO or MgO, respectively.

5 The use of concentrations of  $\text{Fe}_2\text{O}_3$  at the higher end of the specified range tends to produce difficulties in controlling the crystallisation during the conversion of the glass to the glass-ceramic. It is therefore preferred to use not more than 10% by weight of  $\text{Fe}_2\text{O}_3$ .

10 For economic reasons, it is preferred to use not more than 60% by weight in total of BaO and ZnO since the use of concentrations above this level increasingly offsets the economic advantages of using fly ash. Preferably the BaO or ZnO or mixture of BaO and ZnO forms from 2 to 6%, by weight of the composition.

15 The invention also provides a composition suitable for forming into a glass, the composition including the following oxides as essential ingredients:

		by weight
	$\text{SiO}_2$	30—80%
	$\text{Al}_2\text{O}_3$	10—30%
25	$\text{MgO}$	0.5—20%
	$\text{CaO}$	0.5—25%
	$\text{Fe}_2\text{O}_3$	1—13%

30 the  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  together forming at least 90% by weight of the composition, and each oxide being provided as such or in the form of an equivalent amount of at least one precursor therefor, as herein defined; and at least 10% by weight of the composition, calculated as oxides, being provided in the form of fly ash as herein defined.

35 By a precursor for the oxide, as the term is used herein, I mean a material which in the process of fusing the composition, in the course of making the glass or glass-ceramic, will yield or be converted into the oxide.

40 Preferably, the  $\text{MgO}$  and  $\text{CaO}$  are present in combination in the glass-forming compositions in the following ranges (% by weight):

$\text{MgO}$	0.5—5	5—15	8—15
	with	or with	or with
$\text{CaO}$	10—20	1—5	10—20

50 The glass-forming compositions of the invention are of interest in their own right as structural materials, as well as being convertible to glass-ceramic materials in accordance with the invention when including, or modified to include, a nucleating amount of  $\text{TiO}_2$  and optionally at least one other nucleating agent, and the designated amount of BaO and/or ZnO as modifier or inhibitor.

55 An essential component of the compositions of the present invention is fly ash. Fly ashes consist in essence of mixtures of oxides but vary in composition depending upon their

source. Accordingly they are of varying suitability in the compositions of the present invention and lead to glass-ceramic products of varying physical and chemical properties. In general, however, fly ashes are characterised as follows (the percentages being by weight):

$\text{SiO}_2$	36—75 %	
$\text{Al}_2\text{O}_3$	10—39 %	
$\text{Fe}_2\text{O}_3$	1—21 %	70
$\text{CaO}$	0.5—13 %	
$\text{MgO}$	0.2—6 %	
$\text{Na}_2\text{O}$	0.2—6.5 %	
$\text{K}_2\text{O}$	0.2—6.5 %	
$\text{TiO}_2$	0.5—7.5 %	75
$\text{P}_2\text{O}_5$	0.1—0.8 %	
$\text{Mn}_2\text{O}_3$	0.03—0.15 %	
$\text{SO}_3$	0.1—6.0 %	

Loss of ignition 1.0—12% (or possibly more) depending upon the fuel-burning efficiency of the combustion process from which the fly ash is derived.

80 It is to be understood that the above-mentioned materials are present in the fly ash either as such or in a chemically combined form. For example, the  $\text{P}_2\text{O}_5$  will generally be present as phosphate and the  $\text{SO}_3$  as sulphate.

85 While the benefits of using fly ash in accordance with the invention may be obtained even when it forms as little as 10% by weight of the glass- or glass-ceramic-forming composition, it is generally preferred that it forms at least 50% by weight of the composition, and amounts up to 90% by weight, or possibly even more in the case of fly ashes having particularly suitable compositions, may be used.

Mixtures of fly ashes from different sources may be used, if desired.

90 The fly ash will generally be of a fineness such as to pass through a 20 mesh sieve (British Standard). Preferably, however, it will have a fineness such that the particles pass through a 30 mesh sieve, and most preferably through a 60 mesh sieve. Fly ash of such fineness can be employed direct in the formation of the compositions of the invention, without the need for any preparation such as milling, crushing or sieving.

100 Compositions in accordance with the invention may be prepared by direct admixture of the various components. For example, depending on the formation of the fly ash or mixture of fly ashes to be used, the compositions may be formed by incorporating with a quantity of the ash additional quantities of one or more oxides as desired or as necessary to achieve a mixture which has a desired overall composition in which the various oxides are present in the concentrations within the ranges specified.

105 The oxides may be added as such. However, in general it may be more convenient

to substitute for certain of the oxides more readily available precursors which may be thereafter converted to the desired oxides, for example during the heat processing leading to the formation of the glass. By way of example, such precursors may comprise the oxides in chemically combined form, e.g. as in nitrates, carbonates, sulphates or phosphates, or they may comprise oxygen-free forms which are converted to the oxides during the heating process; for example readily oxidisable metals and metal sulphides.

Thus, by way of specific example, the MgO and CaO may conveniently be provided in the form of the respective carbonates, the ZnO may be derived by adding the metal itself to the composition (the metal being oxidized to ZnO during the heating process), and the BaO may be provided as nitrate.

As may be seen from the above analysis, TiO<sub>2</sub> is a usual component of fly ash and thus may conveniently satisfy the requirement for nucleating agent in the glass-ceramic-forming compositions of the invention. Preferably it is used in a concentration of from 0.5 to 10% by weight. However, other nucleating agents may be used in combination with the TiO<sub>2</sub> if desired, examples, with their preferred ranges by weight, being:

	ZrO <sub>2</sub>	up to 6%
	Cr <sub>2</sub> O <sub>3</sub>	up to 4%
	P <sub>2</sub> O <sub>5</sub>	up to 4%
	and preferably at least 0.1%	
35	SnO <sub>2</sub>	up to 3%
	V <sub>2</sub> O <sub>5</sub>	up to 2%
	F <sup>-</sup>	up to 6%
	S <sup>=</sup> and/or SO <sub>4</sub> <sup>=</sup>	up to 2%
	and preferably at least 0.1%	

It will be seen that P<sub>2</sub>O<sub>5</sub> is normally a component of fly ash as phosphate and will therefore generally be unavoidably present in the glass-ceramic-forming composition. However, as a nucleating agent its presence is not undesirable and indeed it is generally preferred to include it.

The other listed optical nucleating agents may be provided, e.g., as Chromite

(Cr<sub>2</sub>O<sub>3</sub> . FeO),

50 Cassiterite (SnSnO<sub>4</sub>), Zircon (ZrSiO<sub>4</sub>), and Cryolite (Na<sub>3</sub>AlF<sub>6</sub>).

Where TiO<sub>2</sub> or P<sub>2</sub>O<sub>5</sub> additional to that provided by the fly ash is desired in the composition, it may be provided, for example, as Rutile (TiO<sub>2</sub>), Ilmenite (FeTiO<sub>3</sub>) or phosphate.

Fe<sub>2</sub>O<sub>3</sub>, which is an essential ingredient of the composition, may also act as a nucleating agent. Where it is required in additional quantities to that provided by the fly ash, it may be added as, for example, Chromite, Ilmenite or the oxide itself.

BaO and ZnO, at least one of which is required as an essential ingredient in the glass-ceramic-forming compositions of the invention, are not normally present in the fly ash and are added to the fly ash. Generally, the BaO is added as nitrate or chloride and the ZnO is added as the oxide itself. Each is preferably present in an amount of from 0.5 to 5.0% by weight. These oxides are not essential in the glass composition of the invention but can be included, if desired, in amounts up to 10% and preferably 2 to 6% by weight.

In addition to the above identified essential ingredients, the glass or glass-ceramic-forming compositions may also include one or more further oxides of metal or metalloid elements. For example they may include one or more of the following optional materials, either as such as in a chemically combined form:

Na <sub>2</sub> O	preferably 0.5 to 5% by weight
K <sub>2</sub> O	preferably 0.5 to 5% by weight
Li <sub>2</sub> O	preferably up to 2% by weight
PbO	preferably up to 5% by weight
MnO <sub>2</sub>	preferably up to 2% by weight
B <sub>2</sub> O <sub>3</sub>	preferably up to 5% by weight

These may act as fluxing agents during melting or as modifiers during the formation of the glass-ceramics by devitrification.

As will be seen, of these optional ingredients, Na<sub>2</sub>O, K<sub>2</sub>O and MnO<sub>2</sub> are generally found in flyashes.

It is also preferred to include As<sub>2</sub>O<sub>3</sub> and/or Sb<sub>2</sub>O<sub>3</sub> in an amount up to 2% by weight as a fining agent, in total.

In general, therefore, the batch will comprise fly ash, sand to provide additional SiO<sub>2</sub> if desired, additional MgO and/or CaO if desired, e.g. as MgO or MgCO<sub>3</sub>, or Ca(OH)<sub>2</sub>, or CaCO<sub>3</sub>, or Dolomite or Calcined Magnesite, and nucleating agent and BaO (e.g. as barium nitrate) and/or ZnO where the glass article is to be converted to a glass-ceramic article. It may also include one or more optional additional ingredients as indicated above and/or other oxides, e.g. one or more of NiO, CoO and oxides of Ge, Ga, Se, Nb and Sb.

In a preferred method of obtaining shaped articles from the glass- or glass-ceramic-forming compositions of this invention, the fly ash and any additional oxides or their precursors, e.g. carbonates or nitrates, are first thoroughly mixed and then melted and maintained in a molten state for a period of time which depends on the composition and quality of the melted glass in known manner. Usually, the temperature will be 1400 to 1550°C and the period of time will be 3 to 8 hours. The melting may be achieved, for example, in a gas fired or electric furnace.

The glass may then be shaped by glass working processes such as casting, rolling, blowing, pressing and drawing.

The glass article so produced may be used as such and without any further treatment, .g. in applications where great strength, abrasion resistance and hardness are not required. In this case, it is not necessary for the composition to contain BaO or ZnO or the TiO<sub>2</sub> nucleating agent although in general the TiO<sub>2</sub> will be present as a normal ingredient of fly ashes.

The glass articles of the invention are of interest in themselves as chemically-resistant products and their strength and hardness will usually be higher than those of ordinary glasses.

Where it is desired to convert the glass article to a glass-ceramic article by controlled devitrification of the glass, this is preferably effected substantially immediately subsequent to the process by which the glass article is formed. The glass article can be stored for conversion to glass-ceramic articles later but in this case it is usually necessary to anneal the glass prior to effecting the devitrification. The temperature of annealing will depend in known manner on the composition of the glass and can readily be determined by simple experiment.

It is to be understood that the glass article to be converted to a glass-ceramic article in accordance with the invention by devitrification must contain nucleating agent and BaO and/or ZnO.

The process for effecting devitrification is now well known. To effect devitrification, the temperature of the glass article is raised, preferably at a rate in the range of approximately 2°C to 10°C per minute, depending upon the composition of the glass and the shape of the article, to just below the softening point to initiate nucleation, and then after a short nucleation the temperature is raised again to the final crystallisation temperature which normally varies from 750°C to 1200°C depending on the composition.

This crystallisation temperature is then maintained for the period of time required to complete crystallisation, usually from ½ hour to 3 hours, and then the crystallised article is cooled down, at least the initial cooling (down to about 600°C) being at a controlled rate of generally not greater than 10°C per minute.

By virtue of the use of fly ash to provide a major proportion by weight of the constituents of the glass-ceramic-forming composition, glass-ceramic articles may be obtained by the invention which are cheap and yet, owing to the advantageous constitution of fly ashes, still have very desirable physical properties comparable, and in some cases superior, to those of known glass-ceramic materials, .e.g. in hardness and strength, resistance to abrasion and chemical attack, and electrical properties such as volume resistivity and electrical breakdown strength. Glass-ceramic materials may also be obtained

in accordance with the invention which have low coefficients of thermal expansion, .e.g. with values for  $\alpha$  in the range  $25-80 \times 10^{-7}$  deg C<sup>-1</sup> at temperatures up to 300°C.

The glass and glass-ceramic materials of the invention may replace traditional materials, .g. glass, ceramics and metals, and can be used in electrical, chemical or mechanical engineering or for laboratory and kitchen ware.

Some particular examples of applications of the glass-ceramic materials of the invention including flooring, wall panels, tiles, linings for chutes and hoppers, staircase steps, roof covering, pipelines, nozzles, jets and guides for fibres and wires, protective coatings against corrosive, chemical or abrasive environments, electrical insulators, spools, and coil formers.

The invention is now illustrated by the following Examples.

#### EXAMPLE 1

A mixture of fly ashes was prepared having the following overall composition by weight:

SiO <sub>2</sub>	42.55%	90
Al <sub>2</sub> O <sub>3</sub>	31.91%	
Fe <sub>2</sub> O <sub>3</sub>	6.74%	
TiO <sub>2</sub>	3.47%	
CaO	3.90%	
MgO	2.20%	95
Na <sub>2</sub> O+K <sub>2</sub> O	2.20%	
SO <sub>3</sub>	0.72%	
P <sub>2</sub> O <sub>5</sub>	0.30%	
Moisture	2.82%	
Loss on Ignition	3.02%	100
Total	99.83	

To 54 parts by weight of this mixture of fly ashes were added:

Sand	25 parts	
MgO	11 parts	105
TiO <sub>2</sub>	5 parts	
BaO	3 parts	
ZnO	2 parts	
As <sub>2</sub> O <sub>3</sub>	0.5 parts	

The composition was mixed and melted at 1520°C for 3 hours. The melt was then formed by pressing into slabs and then placed in a furnace at 680°C. The temperature was then raised at the rate 5°C per min. to 810°C where it was held for a short time and then raised again to 1020°C. At this last temperature the sample was held for 1 hour. The glass-ceramic material so obtained was then allowed to cool, at a rate not exceeding 10°C per minute, down to room temperature.

## EXAMPLE 2

A mixture of fly ashes was prepared having the following overall composition:

5	SiO <sub>2</sub>	47.68%
	Al <sub>2</sub> O <sub>3</sub>	24.60%
	Fe <sub>2</sub> O <sub>3</sub>	8.31%
	TiO <sub>2</sub>	3.92%
	CaO	3.40%
	MgO	1.77%
10	Na <sub>2</sub> O+K <sub>2</sub> O	2.38%
	SO <sub>3</sub>	0.54%
	P <sub>2</sub> O <sub>5</sub>	0.52%
	Moisture	0.61%
	Loss on ignition	6.09%
15	Total	99.82

To 69 parts by weight of this mixture of fly ashes were added:

	Sand	13 parts
20	MgO	11 parts
	TiO <sub>2</sub>	2 parts
	ZrO <sub>2</sub>	2 parts
	BaO	1 part
	ZnO	2 parts
	As <sub>2</sub> O <sub>3</sub>	0.7 parts

25 The composition so obtained was processed as described in Example 1 but using a melting temperature of 1500°C for five hours. The slabs were placed in a furnace at 650°C and the temperature was then raised at the rate of 3°C per minute to 800°C where it was held for a short period and then raised again to 950°C. This temperature was maintained for 1½ hours before allowing the material to cool at a rate not exceeding 10°C per minute.

35 The glass-ceramics of Examples 1 and 2 were of microcrystalline structure, non-deformed and uncracked. They had very good mechanical strength (modulus of rupture up to 1600 kg/cm<sup>2</sup>), were non-porous (water absorption 0.0%) and exhibited a coefficient of thermal linear expansion  $\alpha_{20-300}$  degree C between 25 and 60×10<sup>-7</sup> deg C<sup>-1</sup>. Their densities were in the range 2.6—2.9 g/cc. 45 Their electrical properties are comparable with known glass-ceramic materials. They are generally harder than conventional glasses and exhibit good abrasion resistance.

## WHAT I CLAIM IS:—

50 1. A composition suitable for forming into a glass, the composition including the following oxides as essential ingredients:

		by weight
55	SiO <sub>2</sub>	30—80%
	Al <sub>2</sub> O <sub>3</sub>	10—30%
	MgO	0.5—20%
	CaO	0.5—25%
	Fe <sub>2</sub> O <sub>3</sub>	1—13%

the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, CaO and Fe<sub>2</sub>O<sub>3</sub> together forming at least 90% by weight of the composition, and each oxide being provided as such or in the form of an equivalent amount of at least one precursor therefor, as herein defined; and at least 10% by weight of the composition, calculated as oxides, being provided in the form of fly ash as herein defined.

2. A composition as claimed in claim 1 wherein the Fe<sub>2</sub>O<sub>3</sub> is present in an amount of from 1 to 10% by weight.

3. A composition as claimed in claim 1 or claim 2 containing 0.5—5% by weight of MgO and 10—20% by weight of CaO.

4. A composition as claimed in claim 1 or claim 2 containing 8—15% by weight of MgO and 10—20% by weight of CaO.

5. A composition as claimed in claim 1 or claim 2 containing 5—15% by weight of MgO and 1—5% by weight of CaO.

6. A composition as claimed in any one of claims 1 to 5 further including up to 10% by weight of BaO and/or ZnO.

7. A composition as claimed in claim 6 in which the BaO and/or ZnO forms 2 to 6% by weight of the composition.

8. A composition as claimed in claim 6 in which each of the BaO and ZnO, when both oxides are present, forms 0.5—5% by weight of the composition.

9. A composition suitable for forming into a glass-ceramic, the composition including the following oxides as essential ingredients:

		by weight
	SiO <sub>2</sub>	30—80%
	Al <sub>2</sub> O <sub>3</sub>	10—30%
	MgO	0.5—20%
	CaO	0.5—25%
	Fe <sub>2</sub> O <sub>3</sub>	1—13%
	BaO and/or ZnO	1—10%

and TiO<sub>2</sub> as nucleating agent, optionally together with one or more other nucleating agents;

the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, CaO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and other nucleating agent or agents present, if any, forming at least 90% by weight of the composition, and each oxide being provided as such or in the form of an equivalent amount of at least one precursor therefor, as herein defined; and at least 10% by weight of the composition, calculated as oxides, being provided in the form of fly ash as herein defined.

10. A composition as claimed in claim 9 wherein the Fe<sub>2</sub>O<sub>3</sub> is present in an amount of from 1 to 10% by weight.

11. A composition as claimed in claim 9 or claim 10 in which the BaO and/or ZnO form 2 to 6% by weight of the composition.

12. A composition as claimed in claim 9 or claim 10 in which each of the BaO and

- ZnO, when both oxides are present, forms 0.5 to 5% by weight of the composition.
13. A composition as claimed in any one of claims 9 to 12 containing 10—21% by weight in total of MgO+CaO.
14. A composition as claimed in claim 13 containing 1—6% by weight of one of MgO and CaO and 8—15% by weight of the other of MgO and CaO.
15. A composition as claimed in any one of claims 9 to 14 which includes at least one of the following materials as a nucleating agent in addition to the  $\text{TiO}_2$ :  $\text{ZrO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SnO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{F}^-$ ,  $\text{S}^-$  and  $\text{SO}_4^{2-}$ .
16. A composition as claimed in claim 15 including at least one of the following materials in the concentration indicated:
- |  |           |  |  |
|--|-----------|--|--|
| $\text{ZrO}_2$                         | up to 6%  |  |  |
| $\text{Cr}_2\text{O}_3$                | up to 4%  |  |  |
| $\text{P}_2\text{O}_5$                 | 0.1 to 4% |  |  |
| $\text{SnO}_2$                         | up to 3%  |  |  |
| $\text{V}_2\text{O}_5$                 | up to 2%  |  |  |
| $\text{F}^-$                           | up to 6%  |  |  |
| $\text{S}^-$ and/or $\text{SO}_4^{2-}$ | 0.1 to 2% |  |  |
23. A composition as claimed in any of claims 1 to 22 which further includes at least one of the following oxides:  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$ ,  $\text{MnO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{PbO}$  and  $\text{B}_2\text{O}_3$ , each oxide being provided as such or in the form of at least one precursor thereof, as herein defined.
24. A composition as claimed in claim 23 including at least one of the following oxides in the concentration indicated:
- |                        |           |  |
|------------------------|-----------|--|
|                        | by weight |  |
| $\text{Na}_2\text{O}$  | 0.5 to 5% |  |
| $\text{K}_2\text{O}$   | 0.5 to 5% |  |
| $\text{Li}_2\text{O}$  | up to 2%  |  |
| $\text{PbO}$           | up to 5%  |  |
| $\text{MnO}_2$         | up to 2%  |  |
| $\text{B}_2\text{O}_3$ | up to 5%  |  |
- the oxide being provided as such or in the form of an equivalent amount of at least one precursor thereof, as herein defined.
25. A composition as claimed in any one of claims 1 to 24 including one or both of  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  in an amount up to 2% by weight in total.
26. A composition as claimed in any one of claims 1, 2, 9 and 10 substantially as hereinbefore described and as illustrated in each of the Examples.
27. A glass obtained from a composition as claimed in any one of claims 1 to 26.
28. A glass-ceramic obtained from a composition as claimed in any one of claims 9 to 16 or any of claims 17 to 26 when appendant to any one of claims 9 to 16.
29. A glass-ceramic obtained by controlled devitrification of a glass obtained from a composition as claimed in any one of claims 9 to 16 or any of claims 17 to 26 when appendant to any one of claims 9 to 16.
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